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Title	:	"A Process for the Manufacture of Titanium."

A Process for the Manufacture of Titanium

The present invention pertains to a process for the manufacture of titanium by reduction of titanium tetrachloride with molten alkali or earth alkali metals, or a mixture of these metals.

Titanium has until now essentially been manufactured according to the so-called Kroll process consisting of letting titanium tetrachloride drip down into the molten magnesium. This process with appurtenant apparatus is originally described in US Patent no. 2,205,854. A series of patents has later been granted for various modifications of the original Kroll process. Examples of such patents are:

US Patents nos. 2,564,337; 2,567,837; 2,607,674; 2,621,121; 2,647,826 and British Patent no. 638,840.

More recently the reduction of titanium tetrachloride with sodium has also gained increasing use, and a number of patents has been granted for various processes and apparatus which use sodium as reducing agent. An example of a patent of this type is British Patent no. 717,930, corresponding to Norwegian Patent no. 84,847.

However, for the time being neither the Kroll process nor methods using sodium as reduction agent can produce titanium at prices which allow a general use of the metal as a constructional material, and it is therefore of great importance that experiments for developing improved production processes be carried out.

The present invention relates to a process for the reduction of titanium tetrachloride by means of molten alkali or earth alkali metals, or a mixture of these metals.

The improvements achieved by the present invention are, when compared with known methods and apparatus for the manufacture of titanium by thermal reduction of titanium tetrachloride, for the first that the reaction products by means of the centrifugal force are continuously removed from the reaction zone, whereby the hazard to formation of lower titanium chlorides is eliminated or possibly deminished, and for the second that the process makes the continuous manufacture of titanium possibl .

In US Patent no. 2,395,286 it was previously suggested to use a centrifuge in connection with a process for the manufacture of titanium by alumino-thermal

reduction of titanium dioxide. According to this patent, the titanium resulting from the reduction and which is in a liquid state, is to be separated from the other reaction products by centrifugation. However, as titanium in molten state attacks all known ceramic materials, it is scarcely likely that the process suggested in the said US Patent could deliver a sufficiently pure titanium. In all processes which aim at the manufacture of ductile titanium and where thermal reduction is used, it must be considered to be very important that the reduction is effected at so low a temperature that the titanium does not attack the materials in the reactor.

In the process according to the invention, titanium is manufactured by reduction of titanium tetrachloride with a molten alkali or earth alkali metal, including magnesium, or a mixture of these metals, and the process is carried out in the way that titanium tetrachloride is introduced into the molten reduction agent which is located in a centrifuge rotating with a speed so that the titanium resulting from the reduction and the formed alkali or earth alkali metal chloride are separated from the molten reduction agent thereby that the reaction products by the centrifugal force are pressed against the wall of the centrifuge, whereupon they are removed therefrom.

The centrifuge being used is, according to a first embodiment, cylindrical and provided with a scraper device for the removal of the reaction products. The centrifuge can also according to a further embodiment be given a conical shape so that the reaction products are continuously removed thereby that they glide upwards along the wall of the centrifuge and are then flung out therefrom.

The centrifuge is further suitably heated by means of electrical heating elements enclosed in the wall of the centrifuge. The titanium is continuously or discontinuously charged below or over the surface of the reduction agent in the centrifuge. The reduction agent is also continuously or discontinuously in solid or molten state charged into the centrifuge.

The centrifuge with appurtentant supply lines and optional scraper device is built into a room wherein an inactive atmosphere, e.g. argon, can be maintained. The supply lines and the scraper device as well as thermocouples for the reading of the temperature and electrical conduits for the heating of the centrifuge are gas-tightly passed through the walls of the room in which the centrifuge is situated. The same applies of course to the shaft of the centrifuge as the drive means for the centrifuge is arranged outside the gas-tight room.

In Figures 1a and 2 there are, in s ction, schematically shown two embodiments of apparatus for the carrying out of the process.

A centrifuge *a* with a cylindrical design (Fig. 1a) or conical design (Fig. 2) and which rotates with variable speed on the vertical hollow shaft *f*, contains the reduction agent *b*. The centrifuge is constructed of heat resistant steel covered on its interior with a layer of the same material or a layer of molybdenum, tungsten or tanthalum or of a ceramic material, e.g. aluminium oxide. The exterior of the centrifuge is provided with electrical resistance heating. The resistance wire is covered by a layer of insulation mass. The insulation mass is kept in place by an outer mantel. The supply of electrical energy for the heating is effected through the hollow shaft provided with sliding contacts (these are not shown in Fig. 1a or Fig. 2). Through the tube *c*, which is arranged axially in relation to the centrifuge and which can be moved vertically, the supply of titanium chloride vapour or a mixture of titanium tetrachloride vapour and argon is effected. The lower end of the tube *c* has radially arranged outlet openings. A thermocouple *g* which indicates the temperature in the metal during the reduction is attached to the tube *c*. The supply of reduction agent is effected through the tube *d*. The material of the supply tubes *c* and *d* is heat resistant steel. For the removal of the reaction products, the cylindrically designed centrifuge (Fig. 1a) is provided with a movable scraper *e*. In Fig. 1b, the scraper *e* is drawn seen from the side and from above. The scraper is constructed of heat resistant, perforated steel plate and is designed so that it can glide tightly along the bottom and walls of the centrifuge and collect the reaction products simultaneously with the straining off of the major amount of entrained reduction agent. The whole centrifuge is built in into a gas-tight room constructed of heat resistant steel. This room is provided with passages for the shaft *f*, the supply tube *c* and *d*, the scraper *e*, thermocouple *g* and an outlet tube for argon. The shaft *f*, tube *c* and scraper *e* are movable in gas-tight, cooled bearings. On the bottom of the gas-tight room is a larger opening which permits the emptying of the reaction products.

The process according to the invention will be particularly well suited for a reduction of titanium tetrachlorid with sodium. B cause of this, a more explicit report will be giv n below regarding in what way this reduction can be carried out in the apparatus described in the foregoing.

The following physical data is of importance to the reduction:

	Density	Melting point °C	Boiling point °C
Na	0.97	97.5	880
NaCl	2.165	801	c. 1450
Ti	4.5	1660	-
$TiCl_4$	1.73	-30	136

The process for reducing titanium tetrachloride with sodium will then briefly be as follows:

The gas-tight room containing the centrifuge is filled with argon by means of the supply tube *c*. During the further reduction process a little excess of argon is maintained. The centrifuge is then heated to a temperature somewhat below the temperature at which the reduction is to be effected. Through the tube *d* molten sodium is added, the tube *c* with the thermocouple *g* is lowered into the molten metal and the centrifuge is heated to the temperature at which the reduction is to be carried out. The reduction with sodium is effected at a suitable temperature in the temperature range 100-700°C. The centrifuge is then set into rotation and the mixture of argon and titanium tetrachloride is pressed into the melt through the outlet wholes in the tube *c*. Reduction to metallic titanium takes place momentarily and the reaction products titanium and sodium chloride are by the centrifugal force pressed upwards against the wall of the centrifuge, while novel amounts of titanium tetrachloride and sodium are charged.

The further process will be dependent on which of the two types of centrifuge that is utilised. In a centrifuge with cylindrical design, the supply of titanium tetrachloride and sodium time must be stopped after a certain, the speed of the centrifuge is decreased and the scraper *e* is lowered along the wall of the centrifuge. Under slow rotation the reaction products are scraped off from the wall and bottom of the centrifuge and are emptied of the rim down into the bottom of the surrounding gas-tight room. The reduction process can then be started again.

In a centrifuge of conical design, the reduction proceeds continuously, as the reaction products contaminated with entrained sodium slides upwards along the wall of the centrifuge and are then flung off.

Th titanium manufactured, mixed with sodium chloride and entrained sodium, is coll cted at the bottom of the gas-tight room. In this gas-tight room or in another gas-tight room filled with argon, the excess of sodium is removed thereby

that the mixture is centrifug d at a suitable temperatur , e.g. 150°C, in a centrifuge with cylindrical perforated walls. The sodium removed in this way can be re-used for reduction of titanium chlorid . The titanium mixed with sodium chloride and possible remnants of sodium are removed from the centrifuge, purified by leaching with water and diluted acid and is at last melted down in a voltaic arch furnace.

Pat nt Claim

1. A process for the manufacture of titanium by thermal reduction of titanium tetrachloride by means of molten alkali or earth alkali metals, or a mixture of these metals, characterised in that the reaction is carried out in a centrifuge rotating with such speed that the titanium resulting from the reaction and the formed alkali or earth alkali metal chloride are separated from the molten reduction agent thereby that the reaction products by means of the centrifugal force are pressed against the wall of the centrifuge, whereupon they are removed therefrom.

2. A process according to claim 1, characterised in that the centrifuge is cylindrical and that it for removal of the reaction products is provided with a scraper device.

3. A process according to claim 1, characterised in that the centrifuge has a conical design so that the reaction products are continuously removed thereby that they glide upwards along the wall of the centrifuge and out from the centrifuge.

4. A process according to claims 1 to 3, characterised in that the centrifuge is heated.

5. A process according to claims 1 to 4, characterised in that the centrifuge is built in into a room where an inactive atmosphere is maintained.

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Cited publications: None
One page of drawings (2 figures)

FIG. 1.

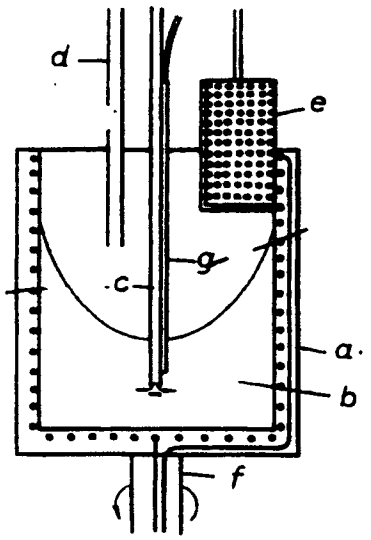

FIG. 2.